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13. ABSTRACT (Maximum 200 words)

This DURIP Grant progress report describes the use of the Silicon Graphics (SGI) ORIGIN 2400 server with eight R12000 CPUs and 512 Megs of RAM for every node (1 node = 2 CPUs). Using this advanced and powerful multiprocessor SGI server, we were able to dramatically speed and further advance our computational Density Functional calculations on CO absorbed on Pt and alloy clusters. Our recent data presented at the ARO Workshop on "Applications of First-Principles-Based Computational Methods to the Design of Electrochemical Power Systems" Berkeley, CA August 31, 2001 included XANES data which showed that the catalyst particles at the anode of fuel cells are metallic.

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RE: Final report – DAAD19-00-1-0095
PI: Eugene Smotkin, Ph.D.

Enclosed please find the Final Report for the above referenced award.

The final official financial report will come to you from our accounting department, Ms. Donna Estler, manager.

If you should have any questions, please do not hesitate to contact me at (312) 567-3035.

Sincerely,

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PROGRESS REPORT

INTRODUCTION

This DURIP Grant progress report describes the use of the Silicon Graphics (SGI) ORIGIN 2400 server with eight R12000 CPUs and 512 Megs of RAM for every node (1 node = 2 CPUs). Using this advanced and powerful multi-processor SGI server we were able to dramatically speed and further advance our computational Density Functional calculations on CO adsorbed on Pt and alloy clusters. Our recent data presented at the ARO Workshop on "Applications of First-Principles-Based Computational Methods to the Design of Electrochemical Power Systems" Berkeley, CA August 31, 2001 included XANES data which showed that the catalyst particles at the anode of fuel cells are metallic. This further justifies are modeling of catalyst particles as metallic. Our previous experimental results include FTIR data of CO adsorbed on Pt based alloys. We observed that the CO stretching frequencies decreased as the mole fraction of Pt decreased in arc-melted alloys. There are a number of factors that can contribute to this phenomenon including coverage effects (dipole-dipole coupling) and electronic effects. The DFT calculations examine electronic effects.

PROCEDURE

All calculations were performed using Jaguar version 4.0 and 4.1 on the Silicon Graphics (SGI) 2400 described before. Jaguar is provided to our group by Schrodinger Corporation under a special agreement. The advantages of this software are:

- runs under multiprocessor environments like the SGI 2400 (pseudo spectral method only).

- uses of the pseudo spectral method that speeds calculations since it runs as $N^{1.5}$ vs. N^3 that conventional fully analytical DFT methods run, where N is the number of atomic basis set used.
- use of the partial Hessian approach that allows us to perform efficient calculations of the Hessian including only atoms that directly involved in CO adsorbance on the Pt, Pt-alloy surface.

The Hamiltonian used was B3LYP non-local spin density method and LACVP basis sets. For each cluster we first determine the optimal spin for ground state configuration (lowest SCF energy) and then this was geometrically optimized. Normal mode calculations were performed using the partial Hessian approach as mentioned above.

PROGRESS

Our primary concern was the effect of the size of the cluster on the CO stretching frequency. Depending on the cluster size and geometry, CO stretching frequency will vary but it will be stabilized when the optimal cluster is found. In order to determine this cluster we started building one-layer pure Pt clusters in (100) arrangement where a single CO was absorbed. All atoms were locked to the interatomic positions as dictated by XRD. Atoms like C, O and the Pt where CO is adsorbed were free to move. By examining Fig. 1 we can see that the one layer case converges to 2174 cm-1 when the size of the cluster is at least 13 Pt atoms and two layers to 2120-2122 cm-1 for least 21 Pt atoms. Although the three-layer case is still in progress, Fig. 1 shows that only one atom is necessary to describe the effect of the third layer thus saving us from unnecessary computations. By alloying the one layer 13 Pt with four Ru atoms the CO C stretching frequency was downshifted from 2174 to 2107 cm-1 as expected by experimental spectra. In this case the Ru atoms are just atomic substitutions for the corresponding Pt atoms in the cluster. In order to avoid edge-effects Ru will not be placed on the boundary of the cluster.

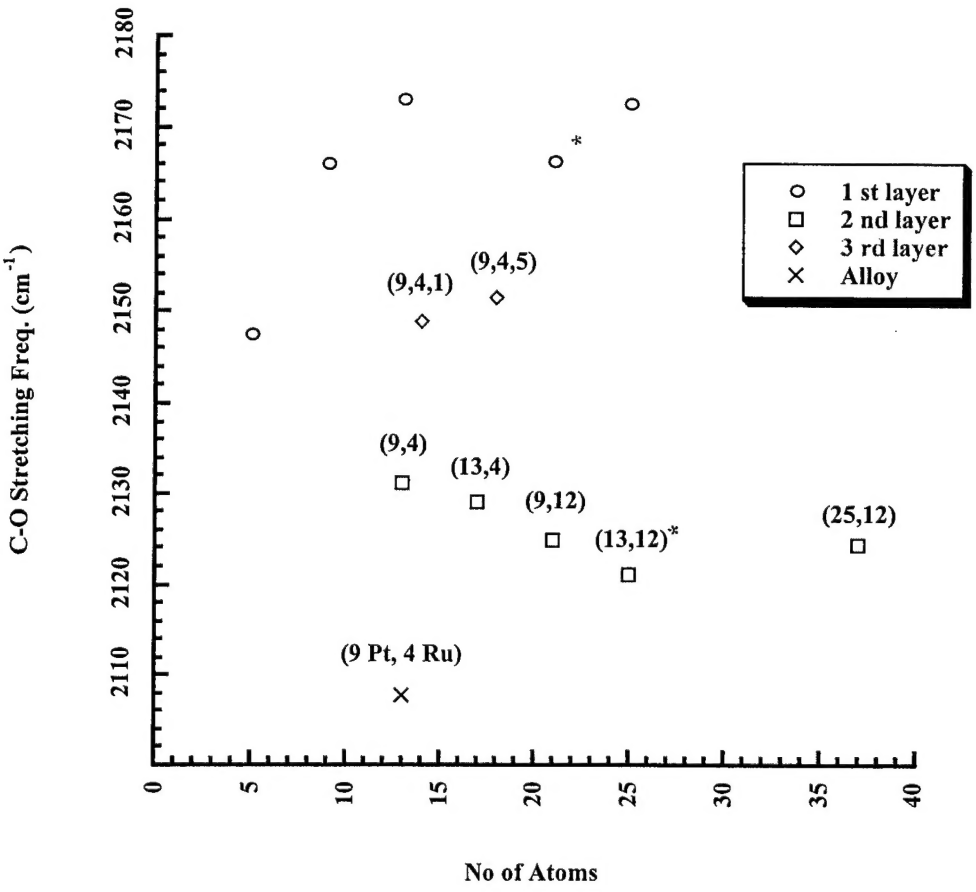

Figure 1. CO stretching normal mode frequency vs. number of atoms for Pt and alloy clusters.

The raw data used to produce figure one are above. The pictures show the cluster structure, the stretching frequency and the carbon-Pt and carbon-oxygen bond distances. The key observation is with the 13 atom single layer clusters. Note the precipitous drop in the CO stretching frequency. This confirms that the electronic effect plays an important role in variations of CO stretching frequencies with Pt content. Further work is being conducted on additional clusters and a stretching frequency versus Pt mole fraction study is underway.

Student Education

One graduate student and one postdoc carried out the above work. The graduate student, Hakim Iddir completed his masters degree and the postdoc, Nicholas Dimakis continues to work on the project.

Future Work

Future work will include simulation of XANES data using quantum mechanical calculations. We will use FEFF 6 to conduct this work. We are now in the process of writing a manuscript on this work, which will include FTIR, XANES and electrochemical data as well as DFT calculations.

From: "Eugene Smotkin" <smotkin@iit.edu>
To: "Domenica G. Pappas" <pappas@iit.edu>
Subject: Platinum Clusters
Date: Mon, 10 Sep 2001 08:16:21 -0700
X-Mailer: Microsoft Outlook IMO, Build 9.0.2416 (9.0.2910.0)
Importance: Normal

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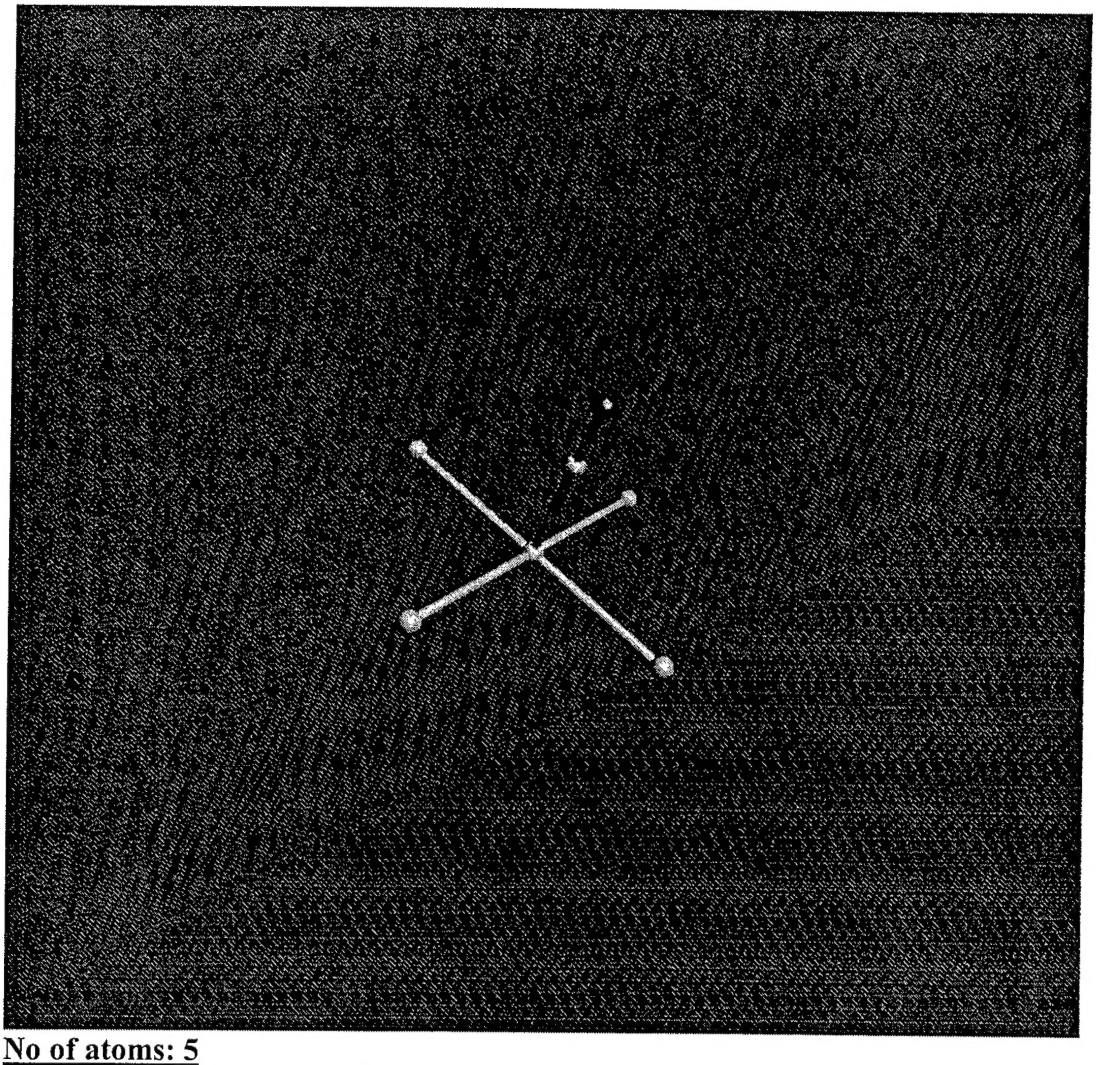
Platinum Clusters

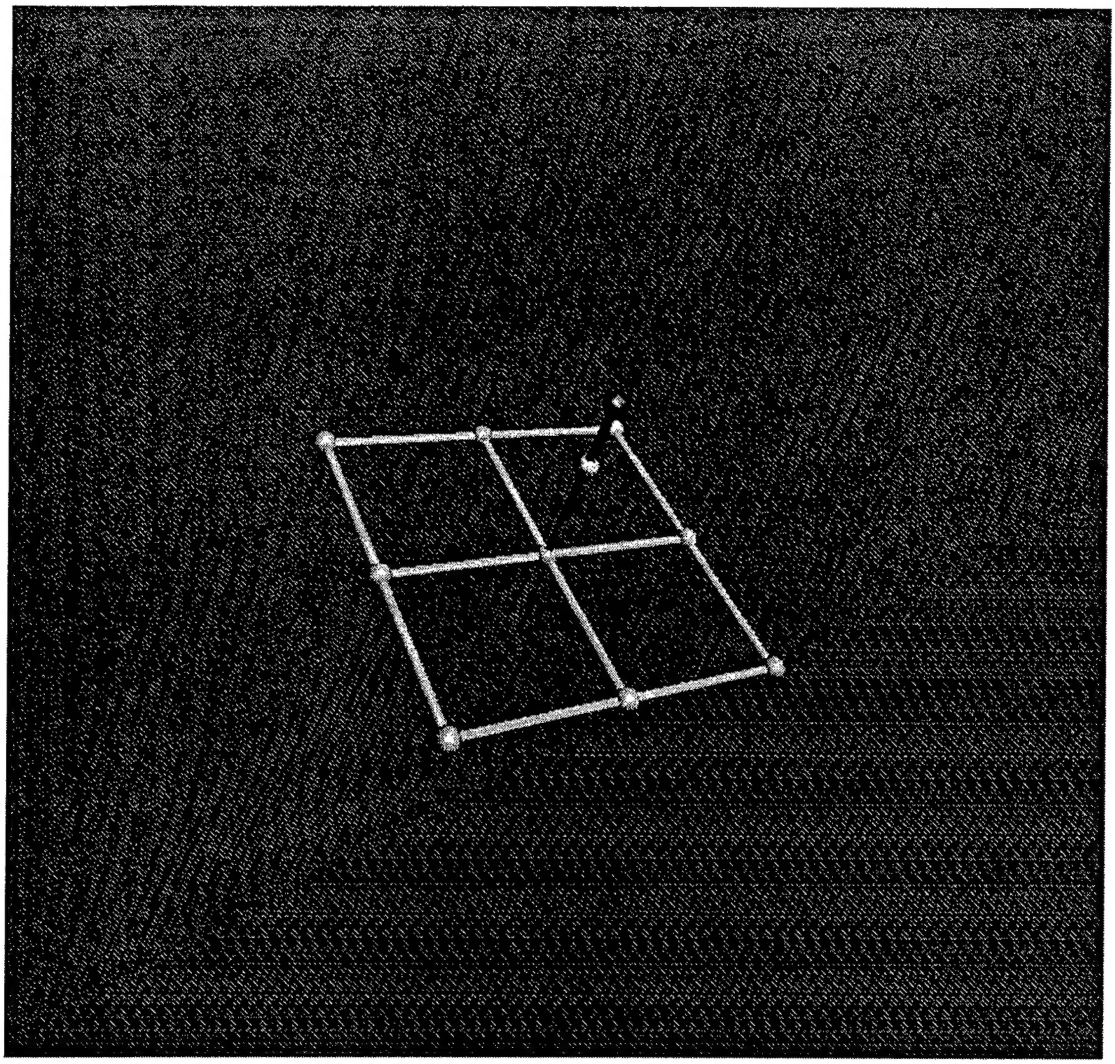
One layer



No of atoms: 5

Pt-C=1.805 Å , C-O=1.150 Å

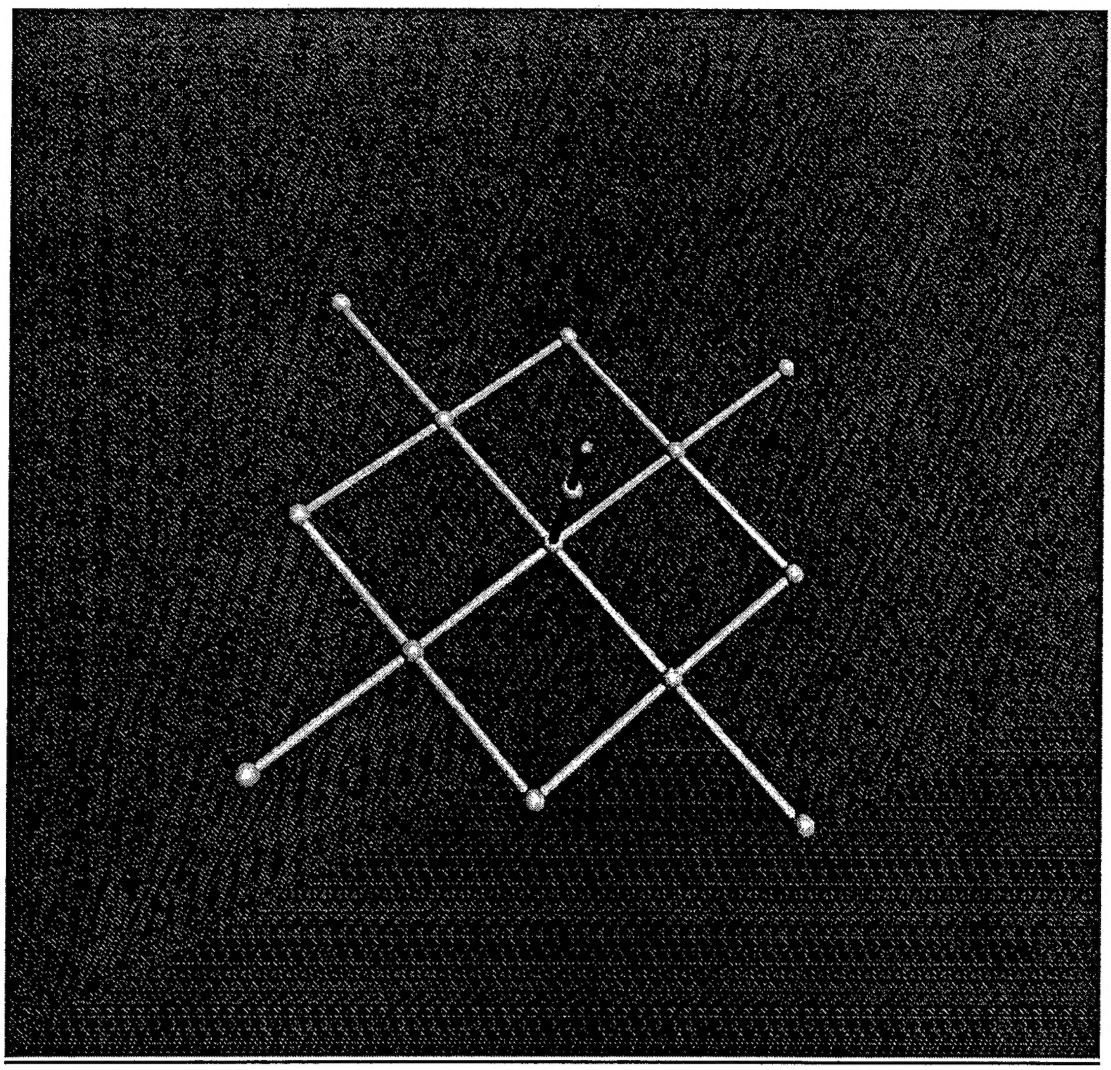
CO Stretching Frequency: 2147.6 cm^{-1}



No of atoms:9

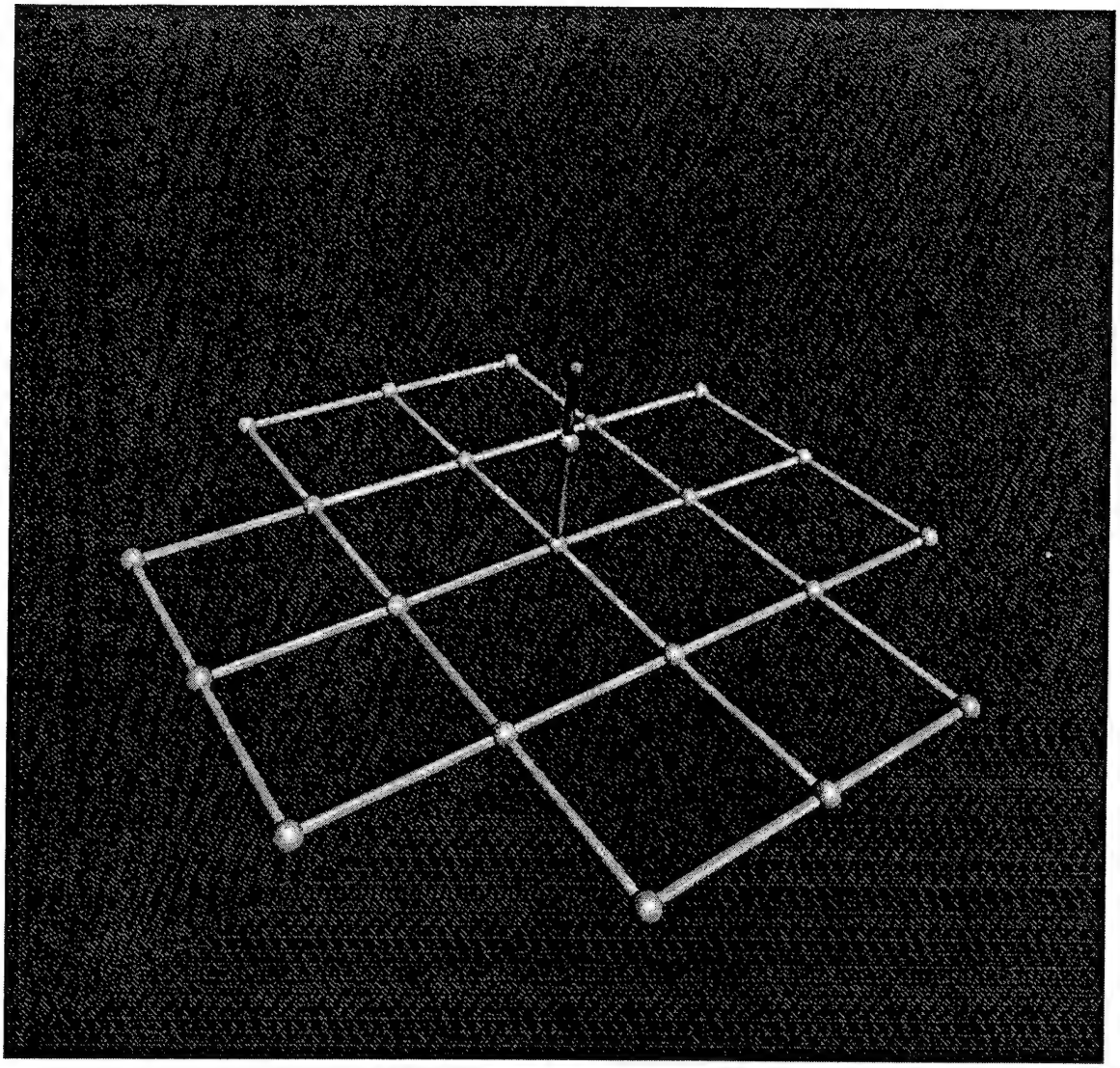
Pt-C=1.80 Å , C-O=1.145 Å

CO Stretching Frequency: 2166.05 cm^{-1}

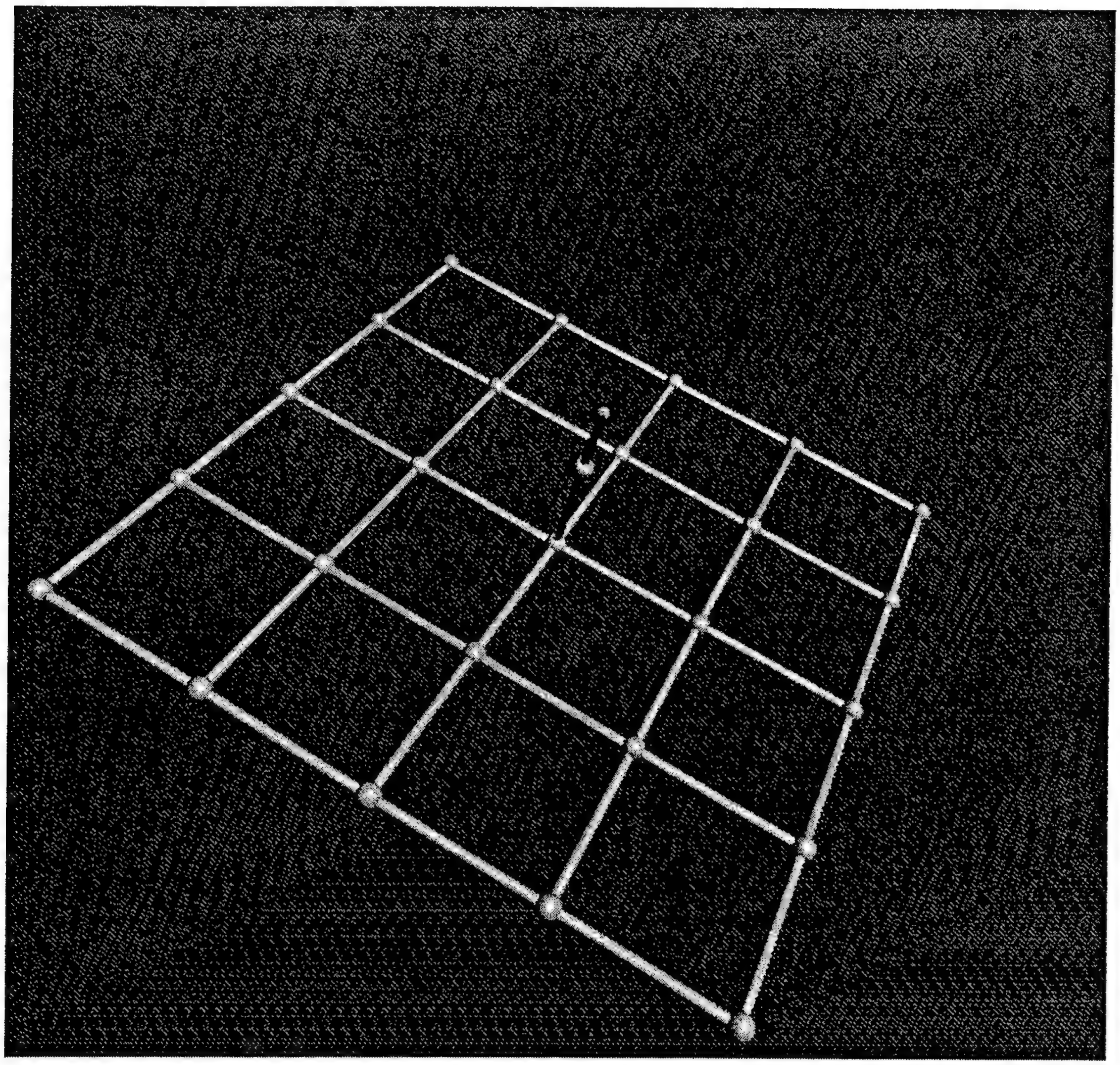


No of atoms:13

CO Stretching Frequency: 2173.0 cm^{-1}



No of atoms:21
Pt-C=1.808 Å , C-O=1.148 Å
CO Stretching Frequency: 2166.16 cm^{-1}

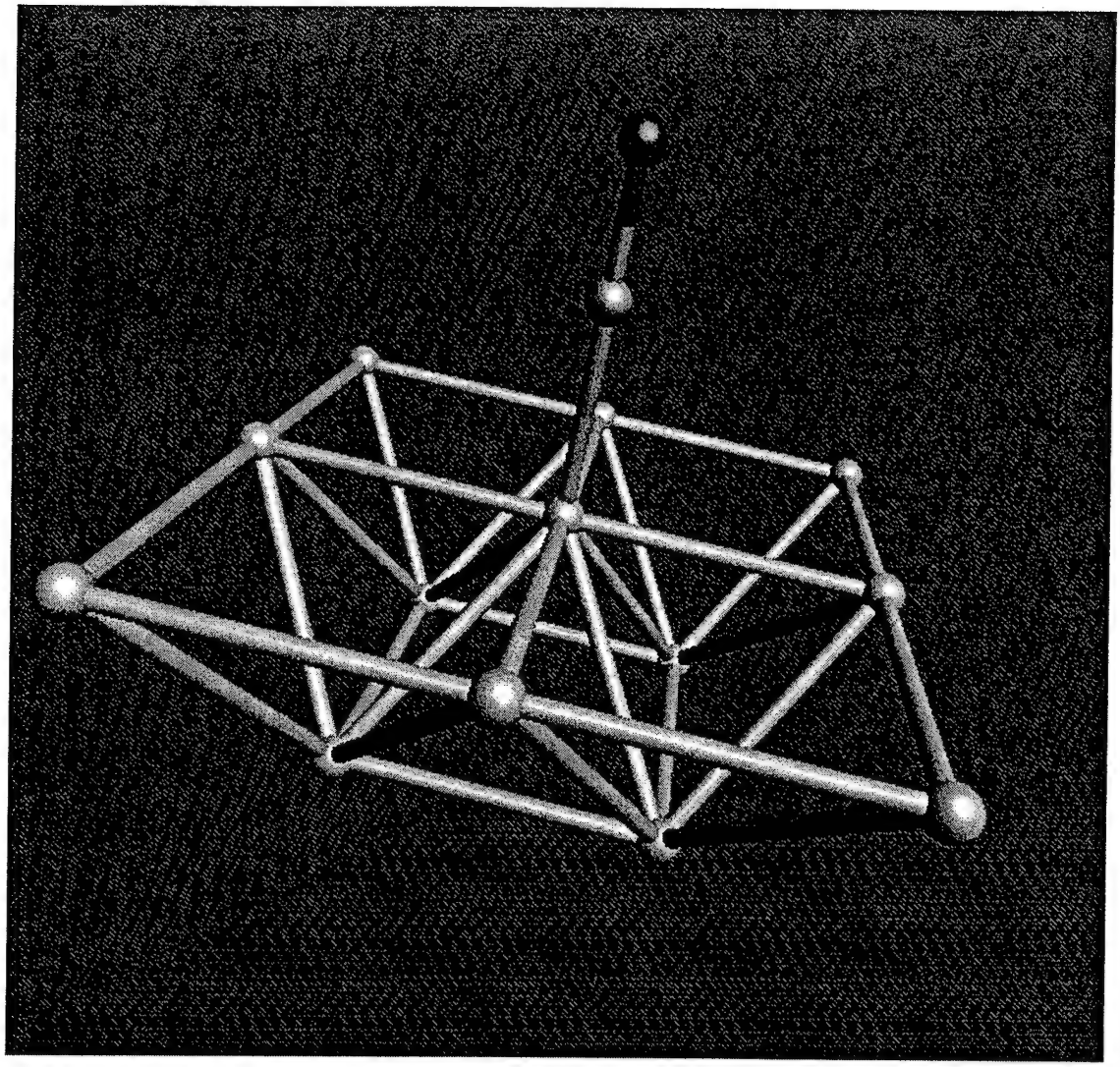


No of atoms:25

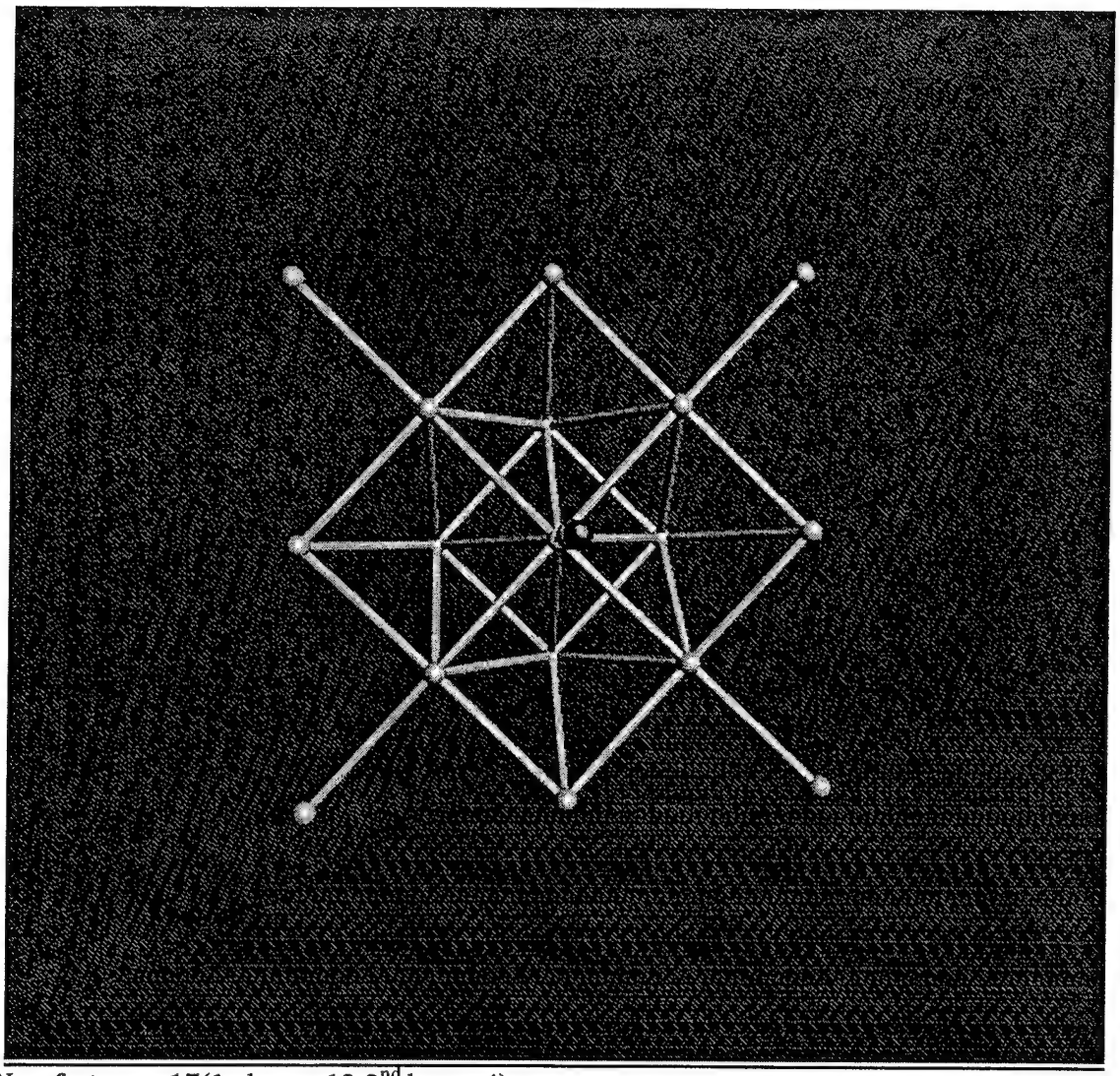
CO Stretching Frequency: 2172.6 cm^{-1}

ONE LAYER HAS CONVERGED TO 2168 cm^{-1}

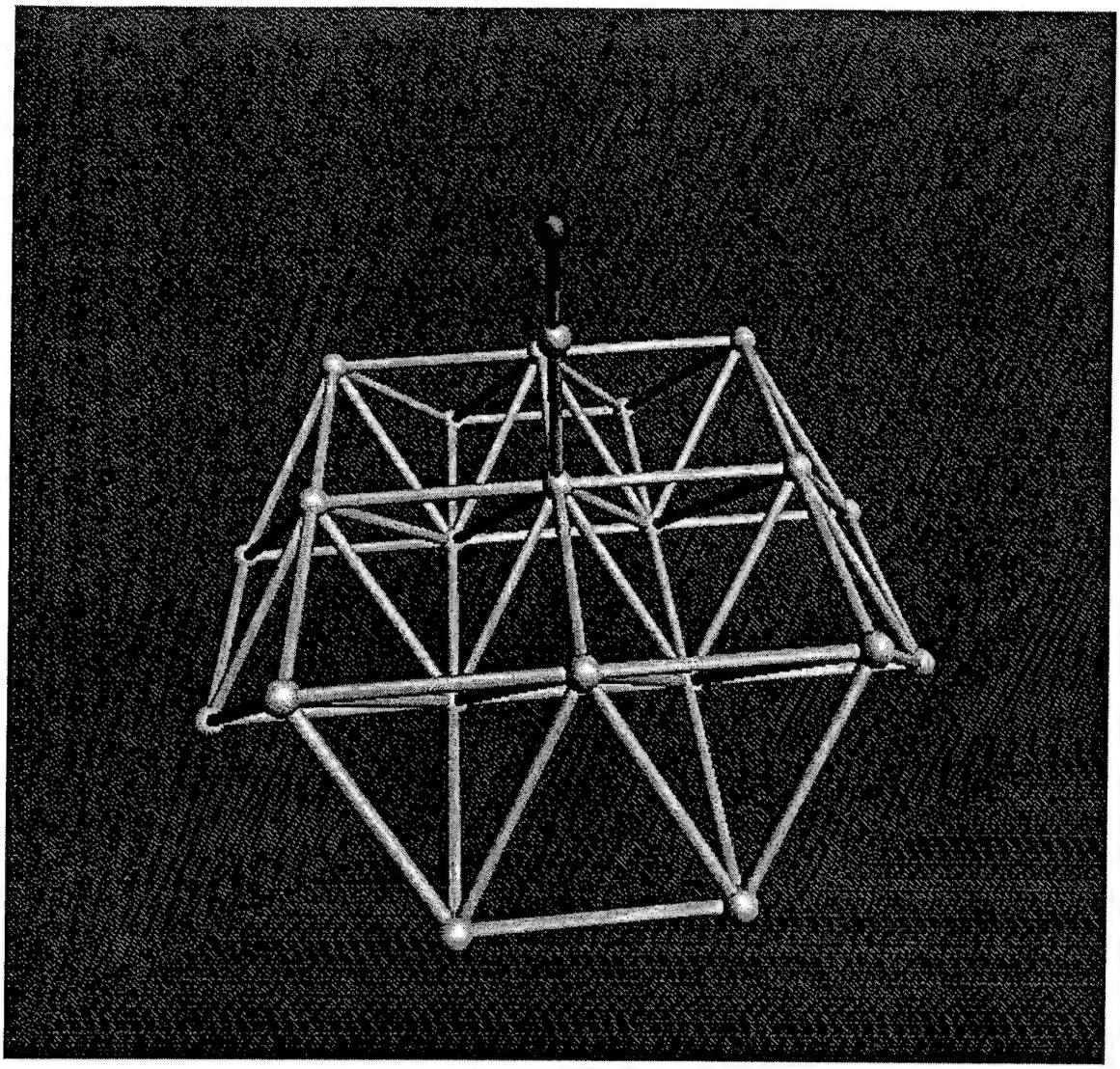
Two Layer



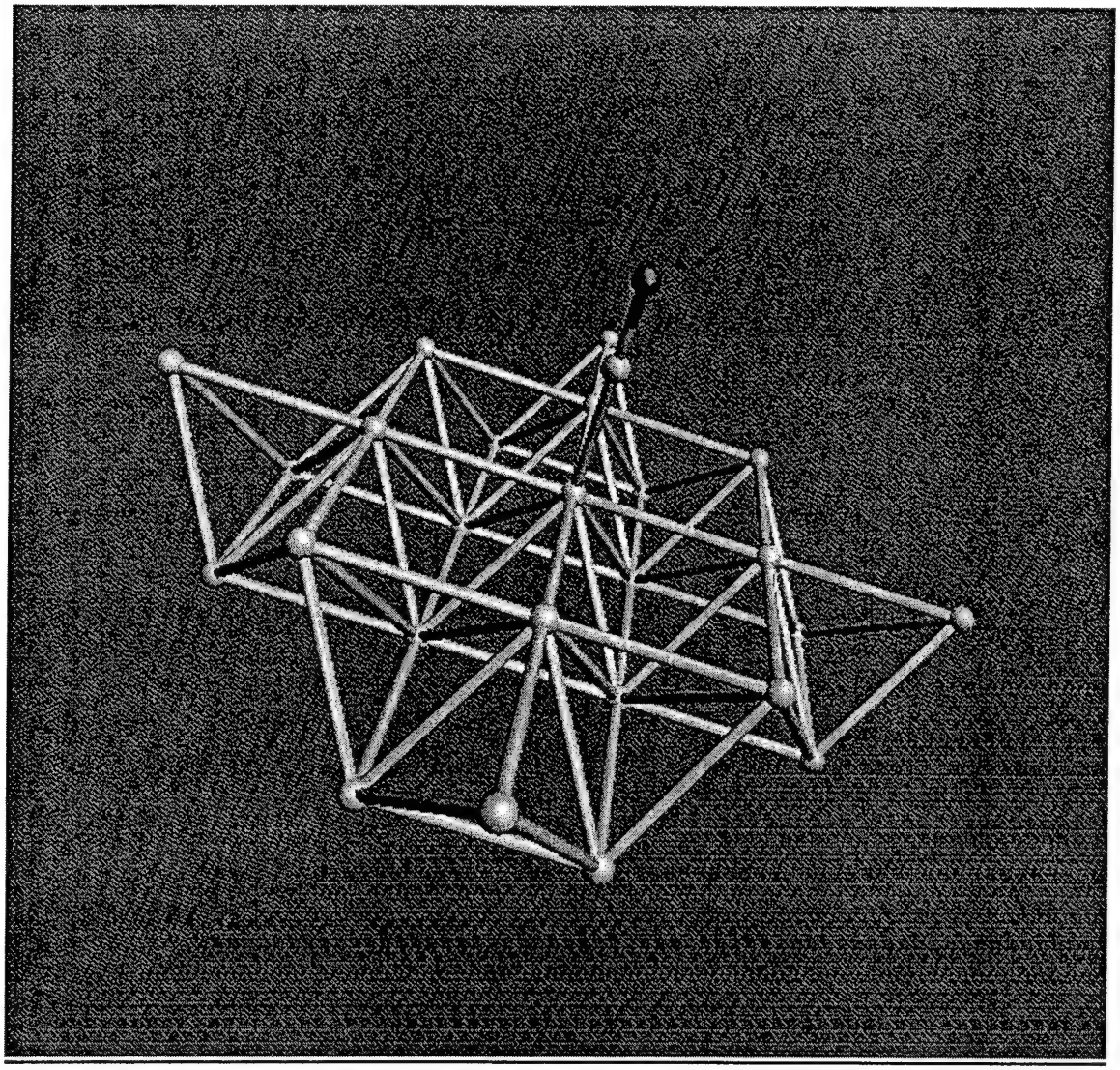
No of atoms: 13 (1s layer: 9, 2nd layer: 4)
Pt-C=1.847 Å , C-O=1.149 Å
CO Stretching Frequency: 2131.07 cm^{-1}



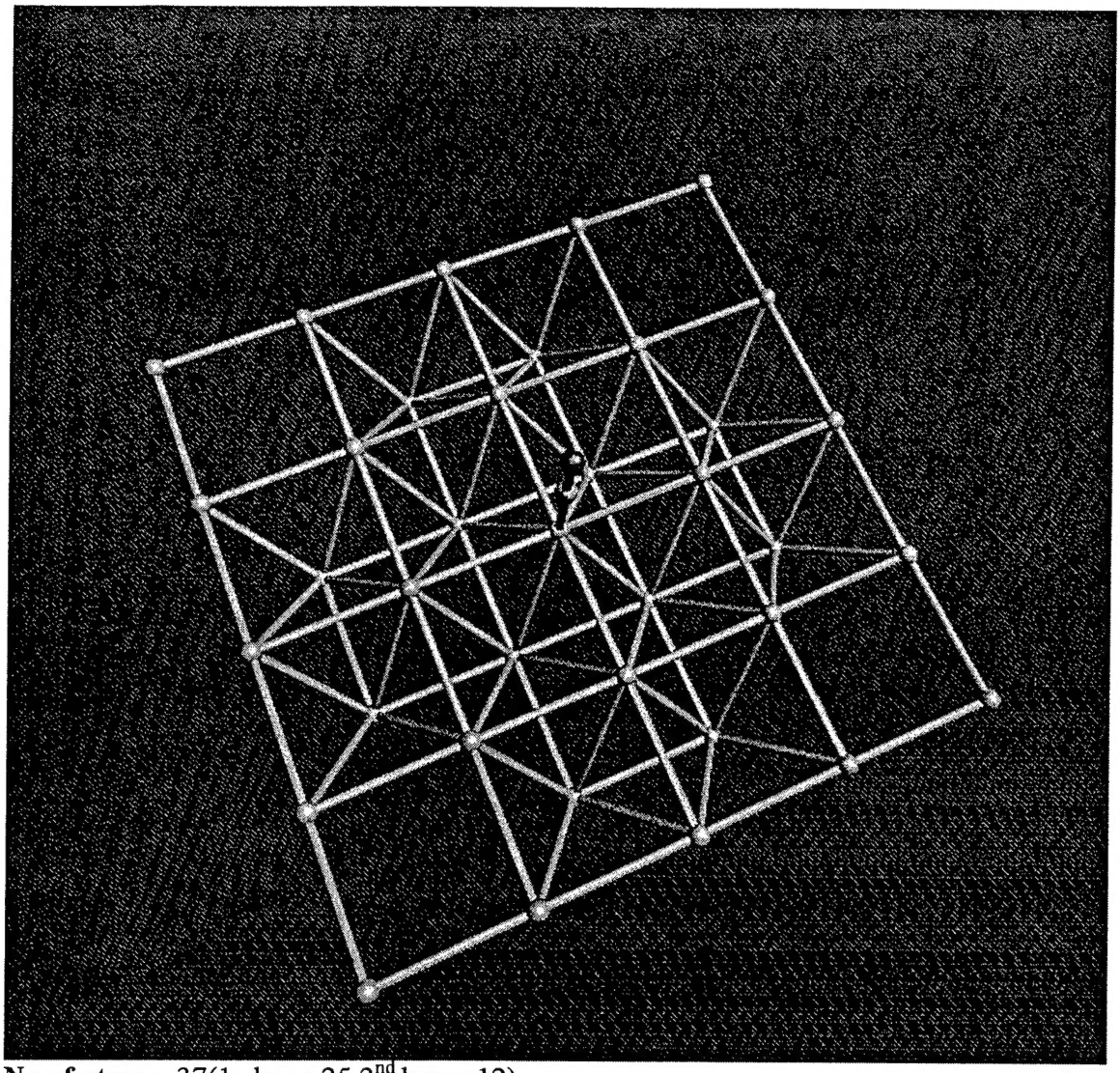
No of atoms: 17(1s layer: 13,2nd layer: 4)
Pt-C=1.846 Å , C-O=1.150 Å
CO Stretching Frequency: 2128.96 cm^{-1}



No of atoms: 21(1s layer:9, 2nd layer: 12)
Pt-C=1.829 Å , C-O=1.152 Å
CO Stretching Frequency: 2124.89 cm^{-1}

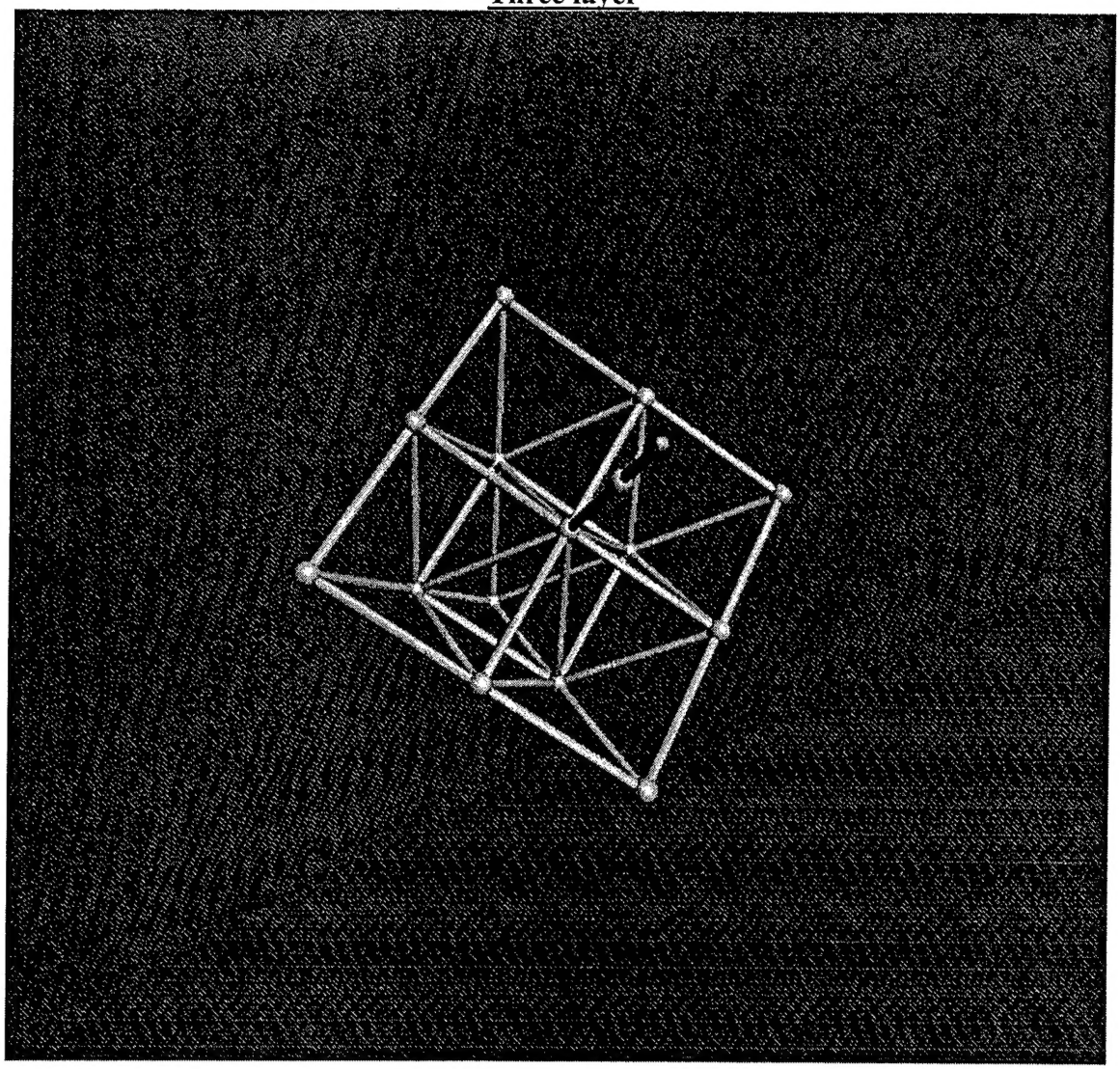


No of atoms: 25(1s layer:13, 2nd layer: 12)
Pt-C= 1.836, C-O=1.151
CO Stretching Frequency: 2121.16 cm^{-1}

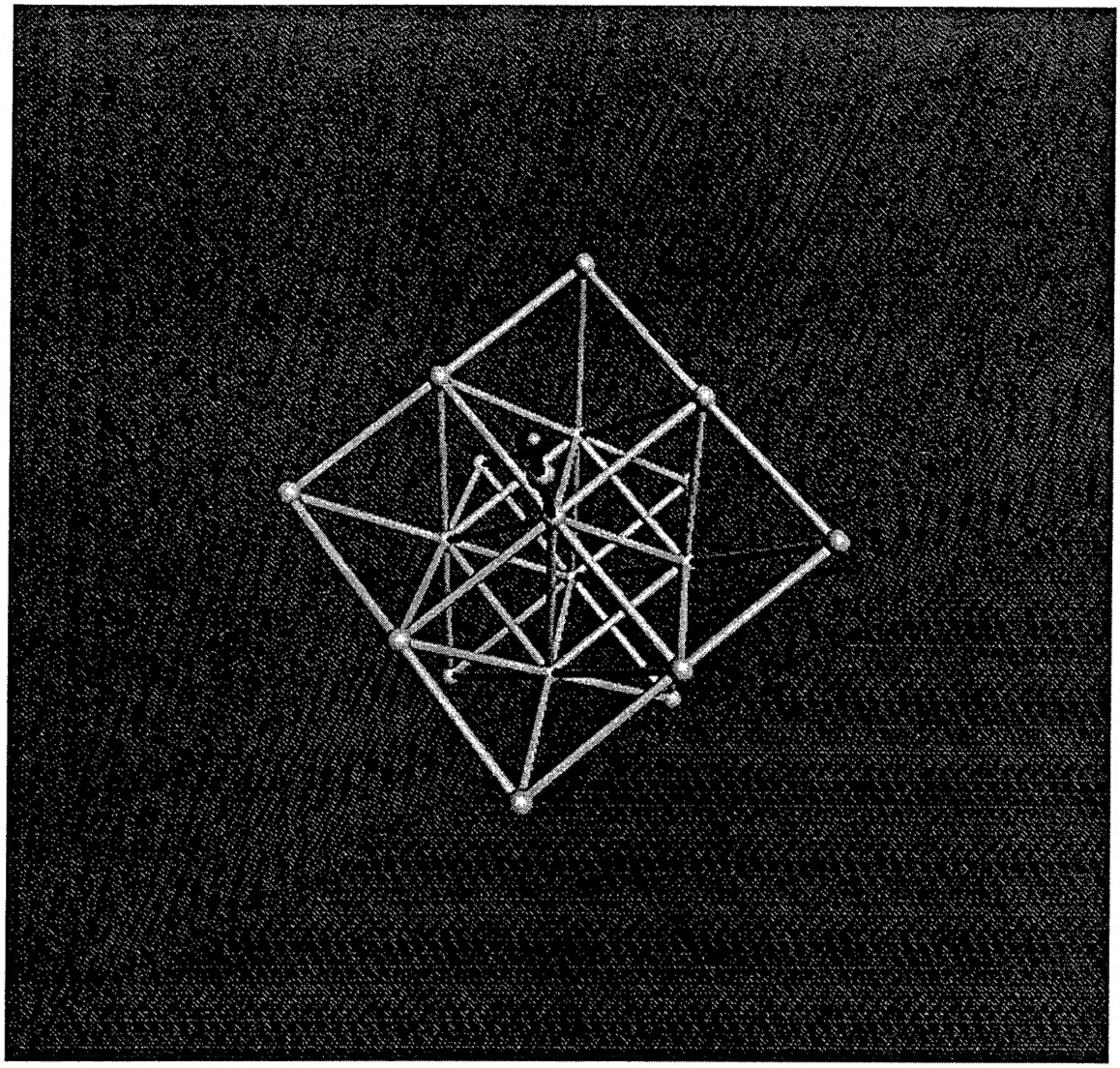


No of atoms: 37(1s layer:25,2nd layer: 12)
Pt-C= 1.848, C-O=1.151
CO Stretching Frequency: 2124.33 cm^{-1}

Three layer

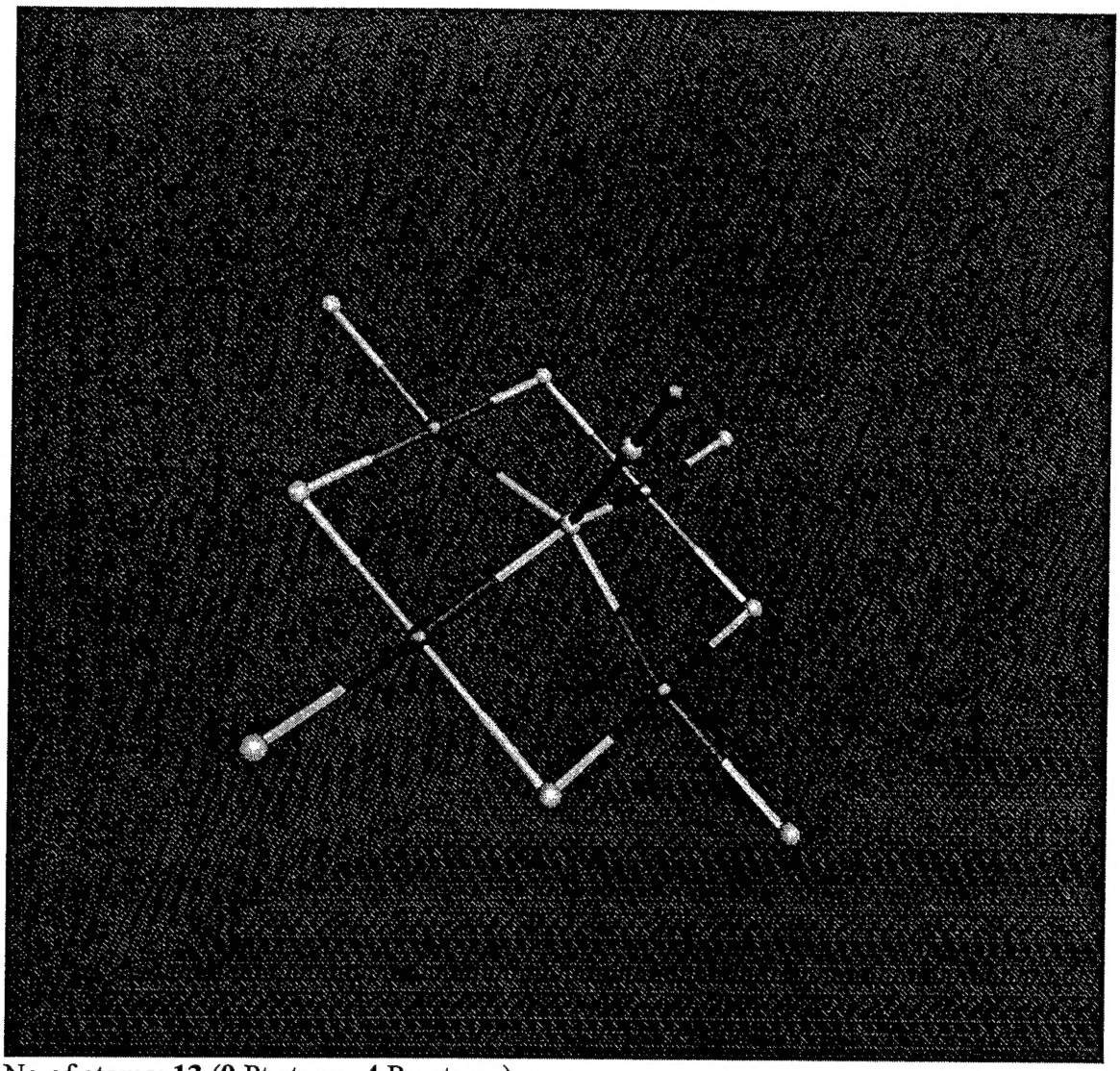


No of atoms: 14(1s layer:**9**,2nd layer: **4**,3rd layer **1**)
Pt-C= 1.827, C-O=1.148
CO Stretching Frequency: 2148.94 cm^{-1}



No of atoms: 18(1s layer:**9**,2nd layer: **4**,3rd layer **5**)
Pt-C= 1.823, C-O=1.148
CO Stretching Frequency: 2151.4 cm^{-1}

Alloy Clusters



No of atoms: **13** (**9** Pt atoms, **4** Ru atoms)
Pt-C= 1.881, C-O=1.151
CO Stretching Frequency: 2107.69 cm^{-1}